

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER

217736US0XPCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/070417

INTERNATIONAL APPLICATION NO.

PCT/JP001/07277

INTERNATIONAL FILING DATE

19 October 2000

PRIORITY DATE CLAIMED

19 October 1999

TITLE OF INVENTION

RUBBER-MODIFIED STYRENIC RESIN, METHOD FOR PRODUCING IT, AND SHEET OF THE RESIN

APPLICANT(S) FOR DO/EO/US

YAZAKI Jun et al.


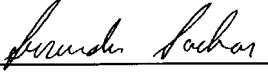
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority/Form PTO-1449
PCT/IB/304/Drawings (1 sheet)
PCT/IB/308

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.01) 10/070417		INTERNATIONAL APPLICATION NO. PCT/JP001/07277		ATTORNEY'S DOCKET NUMBER 217736US0XPCT	
24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	9 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$890.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable) <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$890.00	
				Amount to be refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$890.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
Surinder Sachar Registration No. 34,423  22850			<div style="text-align: center;">  SIGNATURE Norman F. Oblon NAME 24,618 REGISTRATION NUMBER March 15 2002 DATE </div>		

217736US-0X PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
JUN YAZAKI ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: NEW U.S. PCT APPLN :
(BASED ON PCT/JP00/07277)
FILED: HERewith :
FOR: RUBBER-MODIFIED STYRENIC
RESIN, METHOD FOR PRODUCING
IT, AND SHEET OF THE RESIN

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

1. (Amended) A rubber-modified styrenic resin comprising a plurality of particles of a rubbery polymer, said particles dispersed in said resin, wherein said resin has a continuous phase with a weight-average molecular weight (MwL) of between 180,000 and 280,000, and

wherein R¹ and R² each represent a hydrogen atom or an alkyl group having 1 or 2 carbon atoms; and R³ represents an alkyl group having from 1 to 8 carbon atoms.

7. (Amended) The method for producing the rubber-modified styrenic resin as claimed in claim 4, wherein the polyfunctional initiator is 2,2-bis(4,4-di-t-butylperoxycyclohexyl)propane.

8. (Amended) A method for producing the rubber-modified styrenic resin of claim 1, comprising

polymerizing a rubbery polymer and a monomer component consisting essentially of a styrenic monomer in the presence of an unsaturated compound having a plurality of copolymerizing double bonds, wherein an amount of the unsaturated compound is between 50 and 250 ppm relative to the monomer component consisting essentially of a styrenic monomer.

9. (Amended) A rubber-modified styrenic resin sheet prepared by molding the rubber-modified styrenic resin of claim 1.

[illegible]

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Norman F. Oblon
Attorney of Record
Registration No. 24,618



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217736US-0X PCT

Marked-Up Copy Serial No: _____ Amendment Filed on: <u>3-15-2002</u>
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IN THE CLAIMS

--1. (Amended) A rubber-modified styrenic resin [with] comprising a plurality of particles of a rubbery polymer, said particles dispersed in said resin, [dispersed therein, which is characterized in that its] wherein said resin has a continuous phase [has] with a weight-average molecular weight (MwL) [falling] of between 180,000 and 280,000, and [that] wherein the weight-average molecular weight (MwL) and the 1 cm drawdown time (sec) of [the] a resin sheet satisfy the following formula:

$$1 \text{ cm drawdown time (sec)} > (\text{MwL}/10^4) - 4.0.$$

2. (Amended) The rubber-modified styrenic resin as claimed in claim 1, [of which] wherein the continuous phase has a degree of branching of from 0.2 to 1.0 for [its] an absolute molecular weight of 1,000,000 measured in GPC/LALLS.

3. (Amended) The rubber-modified styrenic resin as claimed in claim 1 [or 2, of which] wherein the rubbery polymer content [falls] is between 3 and 12 % by mass.

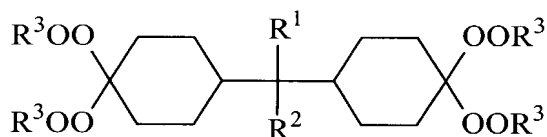
4. (Amended) A method for producing [a] the rubber-modified styrenic resin of [any of claims 1 to 3 by] claim 1, comprising

polymerizing a rubbery polymer and a monomer component consisting essentially of a styrenic monomer in the presence of a polyfunctional initiator, wherein [the] an amount of

the polyfunctional initiator [falls] is between 50 and 500 ppm relative to the monomer component consisting essentially of a styrenic monomer.

5. (Amended) The method for producing a rubber-modified styrenic resin as claimed in claim 4, wherein [the] an amount of the polyfunctional initiator [falls] is between 100 and 500 ppm relative to the monomer component consisting essentially of a styrenic monomer.

6. (Amended) The method for producing [a] the rubber-modified styrenic resin as claimed in claim 4 [or 5], wherein the polyfunctional initiator is a tetrafunctional organic compound of the following [general] formula:



wherein R^1 and R^2 each represent a hydrogen atom or an alkyl group having 1 or 2 carbon atoms; and R^3 represents an alkyl group having from 1 to 8 carbon atoms.

7. (Amended) The method for producing [a] the rubber-modified styrenic resin as claimed in [any of claims 4 to 6] claim 4, wherein the polyfunctional initiator is 2,2-bis(4,4-di-t-butylperoxycyclohexyl)propane.

8. (Amended) A method for producing [a] the rubber-modified styrenic resin of [any of claims 1 to 3 by] claim 1, comprising

polymerizing a rubbery polymer and a monomer component consisting essentially of a styrenic monomer in the presence of an unsaturated compound having a plurality of copolymerizing double bonds, wherein [the] an amount of the unsaturated compound [falls] is between 50 and 250 ppm relative to the monomer component consisting essentially of a styrenic monomer.

9. (Amended) A rubber-modified styrenic resin sheet prepared by molding the rubber-modified styrenic resin of [any of claims 1 to 3] claim 1.--

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JC13 Rec'd PCT/PTO 15 MAR 2002

DOCKET NO.: 217736US0XPCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Jun YAZAKI et al.

SERIAL NO.: NEW U.S. PCT APPLICATION

FILED: HEREWITH

INTERNATIONAL APPLICATION NO.: PCT/JP00/07277

INTERNATIONAL FILING DATE: October 19, 2000

FOR: RUBBER-MODIFIED STYRENIC RESIN, METHOD FOR PRODUCING IT, AND SHEET OF THE RESIN

REQUEST FOR PRIORITY UNDER 35 U.S.C. 119
AND THE INTERNATIONAL CONVENTION

Assistant Commissioner for Patents
Washington, D.C. 20231

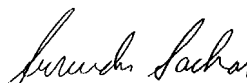
Sir:

In the matter of the above-identified application for patent, notice is hereby given that the applicant claims as priority:

<u>COUNTRY</u>	<u>APPLICATION NO</u>	<u>DAY/MONTH/YEAR</u>
Japan	11-296489	19 October 1999

Certified copies of the corresponding Convention application(s) were submitted to the International Bureau in PCT Application No. PCT/JP00/07277. Receipt of the certified copy(s) by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

Respectfully submitted,
OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
Attorney of Record
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DESCRIPTION

RUBBER-MODIFIED STYRENIC RESIN, METHOD FOR PRODUCING IT, AND SHEET OF THE RESIN

TECHNICAL FIELD

The present invention relates to a rubber-modified styrenic resin and a method for producing it, and also to a sheet of the rubber-modified styrenic resin. More precisely, the invention relates to a rubber-modified styrenic resin having good thermoforming stability and suitable to molding materials for sheets, to a method for producing it, and to a sheet of the rubber-modified styrenic resin.

BACKGROUND ART

As having good mechanical properties such as good impact strength and having good moldability, rubber-modified styrenic resins with a rubbery polymer therein have heretofore been used widely in the art by molding them into sheets followed by further working the resin sheets into secondary products such as wrapping or packaging containers for edibles and daily necessities. Briefly, the resins are molded through extrusion into resin sheets, and the resin sheets are thermoformed in vacuum or under pressure into secondary products.

When the rubber-modified styrenic resin sheet is heated for thermoforming it, it is softened under heat and becomes thermoformable. With the lapse of time, however, the thus-softened sheet often melts to draw down. If the softened

resin sheet draws down too rapidly, the thermoformable time for it shall be shortened and, as a result, stable production of thermoformed products from it will be difficult. In addition, the resin sheet having drawn down too much will reach heaters, and the thermoformed products from it will have a bad appearance.

For prolonging the time to be taken by such a thermosoftened, rubber-modified styrenic resin sheet before it draws down, it is known that increasing the molecular weight of the continuous phase of the rubber-modified styrenic resin is effective. However, merely increasing the molecular weight of the continuous phase of the rubber-modified styrenic resin is problematic in that the productivity of the resin sheets is lowered as the fluidity of the starting resin is low.

In that situation, it is desired to develop a rubber-modified styrenic resin, of which the advantages are that the productivity in molding it into sheets is not lowered and that the thermoforming time for the resin sheets is satisfactorily long, and also to develop a method for producing the resin.

The object of the present invention is to provide a rubber-modified styrenic resin of which the physical properties are enough for ensuring a satisfactorily long time for thermoforming the resin sheets, to provide a method for producing the resin, and to provide a rubber-modified styrenic

[illegible]

E. coli

ppm relative to the monomer component consisting essentially of

BRIEF DESCRIPTION OF THE DRAWING

A: sheet displacement,

B: 1 cm drawdown time,

C: time,

resin will lose stiffness intrinsic to styrenic resins. With its rubbery polymer content falling within the defined range, the modified resin has well-balanced stiffness and impact resistance.

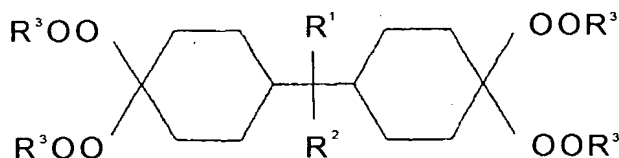
The styrenic resin that forms the continuous phase of the rubber-modified styrenic resin of the invention may be prepared by polymerizing or copolymerizing a monomer component which consists essentially of a styrenic monomer. The styrenic monomer includes, for example, styrene, α -substituted alkylstyrenes such as α -methylstyrene, etc.; nucleus-substituted alkylstyrenes such as p-methylstyrene, p-tert-butylstyrene, etc.; nucleus-substituted halogenostyrenes such as p-chlorostyrene, etc. One or more of these styrenic monomers may be used either singly or as combined.

Comonomers copolymerizable with the above-mentioned styrenic monomers include, for example, vinylic compounds such as acrylonitrile, acrylic acid, methacrylic acid, maleic acid, fumaric acid, maleic anhydride, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, etc.; and also maleimide, nucleus-substituted maleimides, etc. One or more of these comonomers may be used either singly or as combined.

The polyfunctional initiator to be used in the method may have any chemical structure, including trifunctional or tetrafunctional organic compounds, etc. For example, preferred are tetrafunctional organic compounds such as those proposed in Japanese Patent Laid-Open Nos. 125106/1993 and 178920/1993. In these laid-open publications, the tetrafunctional organic compounds disclosed are used for producing rubber-modified styrenic resins of high durability, and the amount of the compound to be in the polymerization system therein is around 2,000 ppm or so relative to the styrenic monomer to be polymerized in the presence of the compound. However, the amount of the polyfunctional initiator to be in the method of the present invention for producing rubber-modified styrenic resins, which are for sheets having good thermoforming stability, is specifically defined to fall between 50 and 500 ppm relative to the monomer component consisting essentially of a styrenic monomer, as so described hereinabove.

As the polyfunctional initiator for use herein, especially preferred are tetrafunctional organic compounds of

the following general formula:



wherein R^1 and R^2 each represent a hydrogen atom or an alkyl group having 1 or 2 carbon atoms; and R^3 represents an alkyl group having from 1 to 8 carbon atoms. The alkyl group for R^1 and R^2 includes a methyl group and an ethyl group; and the alkyl group for R^3 includes a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl, an n-pentyl group, an isopentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, etc.

The tetrafunctional organic compounds of the general formula include, for example, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane, 2,2-bis(4,4-di-tert-hexylperoxycyclohexyl)propane, 2,2-bis(4,4-di-tert-octylperoxycyclohexyl)propane, etc. Of those, especially preferred is 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane.

In the method for producing the rubber-modified styrenic resin by polymerizing or copolymerizing a rubbery polymer with a styrenic monomer or with a combination of a

styrenic monomer and its comonomer, in the presence of an unsaturated compound having a plurality of copolymerizing double bonds, the amount of the unsaturated compound falls between 50 and 250 ppm relative to the monomer component consisting essentially of a styrenic monomer.

In this method, the amount of the unsaturated compound is defined to fall between 50 and 250 ppm relative to the monomer component consisting essentially of a styrenic monomer. This is because, if the amount of the unsaturated compound to be in the polymerization system is smaller than 50 ppm, the branched structure introduction into the polymer chain of the rubber-modified styrenic resin produced will be unsatisfactory, and the drawdown resistance of the resin sheet will be poor when the sheet is thermoformed. On the other hand, if the amount of the unsaturated compound is larger than 250 ppm, the branched structure introduction into the polymer chain of the rubber-modified styrenic resin produced will be too much. If so, the resin will be readily gelled.

The unsaturated compound suitable for use herein includes non-conjugated divinyl compounds such as divinylbenzene, etc.; and polyacrylates such as ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, tetramethylolmethane tetraacrylate, etc. One or more of these unsaturated compounds may be used either singly or as combined.

Regarding the polymerization mode in producing the

In producing the rubber-modified styrenic resin, the polyfunctional initiator or the unsaturated compound having a plurality of copolymerizing double bonds may be uniformly mixed with a monomer component consisting essentially of a styrenic monomer and containing a rubbery polymer dissolved therein, before the monomer component is fed into a polymerization reactor; or it may be fed into a polymerization reactor that contains the starting monomer component having been fed therinto, all at a time or portionwise at different times; or it may be fed therinto after the degree of conversion into polymer in the reactor has reached 20 to 40 %.

In the method of producing the rubber-modified styrenic resin, the temperature in the polymerization reactor and the amount of the chain transfer agent to be fed thereinto are so controlled that the continuous phase of the resin produced could have a weight-average molecular weight (M_{wL}) falling between 180,000 and 280,000. More preferably, they are so

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$$MwL = \Sigma(WiMi) / \Sigma(Wi)$$

wherein W_i indicates the weight fraction of the eluate volume (V_i); and M_i indicates the molecular weight of the eluate volume (V_i).

In producing the rubber-modified styrenic resin by polymerizing a rubbery polymer and a monomer component consisting essentially of a styrenic monomer, a predetermined amount of a polyfunctional initiator or a unsaturated compound having a plurality of copolymerizing double bonds is added to the reaction system, by which a branched structure is introduced into the polymer chain of the resin produced. Preferably, the branched structure introduction into the polymer chain falls between 0.2 and 1.0 in terms of the degree of branching in the polymer chain having an absolute molecular weight measured in GPC/LALLS of 1,000,000.

The absolute molecular weight (M_B) is measured in GPC/LALLS, as in the Examples mentioned hereinunder. For example, the scattered light photometer to be used is Toso's Model LS-8000; the RI detector is Toso's Model RI-801; the column is Shodex-A806M; the solvent is tetrahydrofuran; the sample flow rate is 1.0 ml/min; the sample temperature is 35°C; the sample amount introduced into the column is 100 μ l; and the sample concentration is 0.2 g/100 ml. The degree of branching, $n_{1,000,000}$ for the absolute molecular weight (M_B) measured in GPC/LALLS of 1,000,000 is calculated according to

the method described in J. Chem. Phys., Vol. 17, p. 1301 (1949) and J. Appl. Polym. Sci., Vol. 33, p. 1909 (1987). In this, the value of the following formula:

$$g = (M_L/M_B)^{1.138}$$

is obtained from the linear molecular weight (M_L) and the absolute molecular weight (M_B) obtained in the manner as above. With that, the degree of branching, $n_{1,000,000}$ for the absolute molecular weight (M_B) of 1,000,000 is obtained according to the following formula:

$$g = 1/n_{1,000,000} \times \ln(1 + n_{1,000,000}).$$

In the method for producing the rubber-modified styrenic resin, it is desirable that the polymerization condition is so controlled that the particles of the rubbery polymer dispersed in the resin produced have an area-average particle size falling between 1.5 and 4 μm . This is because, if the area-average particle size of the rubbery polymer particles dispersed in the resin is smaller than 1.5 μm , the sheet impact strength of the resin sheet prepared by molding the resin will be low; but if larger than 4 μm , the surface gloss of the resin sheet will be low.

To mold the rubber-modified styrenic resin into sheets, employable is any ordinary extrusion molding method generally used in the art for molding rubber-modified styrenic resins. In the method of molding the resin into sheets, any ordinary lubricant, antistatic agent, antioxidant, heat stabilizer,

pigment, dye, UV absorbent, and plasticizer may be added to the resin. For enhancing the impact resistance of the resin sheets, an additional rubbery polymer may be added to the resin by kneading them.

The resin sheets prepared by molding the rubber-modified styrenic resin in the manner as above can be thermoformed in vacuum or under pressure into secondary-worked products, for example, into wrapping or packaging containers for edibles and daily necessities.

The method for evaluating the drawdown resistance of the rubber-modified styrenic resin sheets is described. A resin sheet sample having a thickness of 0.5 mm is prepared. This is fitted in a frame having a size of 235 mm × 235 mm, and heated by upper and lower heaters at a heating rate of 180°C/min. Being thus heated, the sheet sample is displaced as in Fig. 1 that indicates the relationship between the sheet displacement and the heating time. Concretely, the sheet is finely waved just after the start of heating, then once draws down, but immediately shrinks back to be flattened. With being further heated, the sheet again draws down. In this stage, the time (sec) before the center of the sheet has drawn down by 1 cm based on the shrink-back point of the sheet is measured, and this is defined as the 1 cm drawdown time (sec) of the sheet tested. For evaluating the drawdown resistance of the rubber-modified styrenic resin sheet, referred to is the 1 cm

drawdown time (sec) of the sheet measured in the manner as described herein. This is based on the fact that the time within which the sheet is thermoformable corresponds to the time taken by the sheet having once shrunk back before its center draws down by 1 cm.

Of the rubber-modified styrenic resin of the invention, the continuous phase has a weight-average molecular weight (MwL) falling between 180,000 and 280,000, and after the resin has been formed into a sheet, the resin sheet satisfies the following formula that indicates the relationship between the 1 cm drawdown time (sec) of the sheet and the weight-average molecular weight (MwL) of the continuous phase of the resin:

$$1 \text{ cm drawdown time (sec)} > (\text{MwL}/10^4) - 4.0.$$

In case where the weight-average molecular weight (MwL) of the continuous phase of the rubber-modified styrenic resin is within a relatively high region, falling between 220,000 and 280,000, the 1 cm drawdown time of the resin sheet well satisfies the above-mentioned formula. However, in case where the weight-average molecular weight (MwL) of the continuous phase of the rubber-modified styrenic resin is within a relatively low region, falling between 180,000 and 220,000, it is desirable that the resin is so controlled that the 1 cm drawdown time of the resin sheet satisfies the following formula:

$$1 \text{ cm drawdown time (sec)} > (0.5 \times \text{MwL}/10^4) + 7.0.$$

The invention is described in more detail with reference to the following Examples.

(1) Production of rubber-modified styrenic resin:

To a styrene solution containing 7.0 % by mass of a rubbery polymer, polybutadiene rubber [Ube Kosan's BR15HB], added were 350 ppm, in terms of its pure product and based on styrene, of a polyfunctional initiator, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane [Kayaku Akuzo's Perkadox 12], 120 ppm, based on styrene, of a chain transfer agent, n-dodecylmercaptan [from Nippon Yushi], and 500 ppm, based on the total of the starting materials, of an antioxidant [Ciba-Geigy's Irganox 245].

The starting solution thus prepared was continuously

fed into a first polymerization reactor of a type for complete admixture having a capacity of 20 liters (its inside was kept at 100°C) at a feed rate of 20 liters/hr. Next, the polymer formed in the first polymerization reactor was led into a second polymerization reactor of a type for complete admixture having a capacity of 20 liter, then into a third, plug-assisted flow polymerization reactor having a capacity of 30 liters, and finally into a fourth, plug-assisted flow polymerization reactor having a capacity of 30 liters in that order. In these, the polymerization temperature was kept falling between 105°C and 180°C, and the starting solution was polymerized to attain a final conversion of at least 70 %.

In the first polymerization reactor of a type for complete admixture, a double helical stirrer was used and kept rotating at 250 rpm; in the second polymerization reactor of a type for complete admixture, a double helical stirrer was used and kept rotating at 70 rpm at 130°C; in the third, plug-assisted flow polymerization reactor, the inlet temperature was 135°C and the outlet temperature was 140°C; and in the fourth, plug-assisted flow polymerization reactor, the inlet temperature was 145°C and the outlet temperature was 150°C. The final conversion was 72 %.

After having been thus polymerized, the resulting reaction product was led into a vacuum degassing reactor heated at 240 to 250°C, in which the volatile components including

the non-reacted monomer and the solvent were removed from the product to obtain a rubber-modified styrenic resin.

The continuous phase of the rubber-modified styrenic resin obtained herein had a linear weight-average molecular weight (MwL) of 240,000, measured according to the method described hereinabove. It had a degree of branching of 0.5 for its absolute molecular weight (M_B) of 1,000,000 measured in GPC/LALLS.

(2) Production of rubber-modified styrenic resin sheet:

To the rubber-modified styrenic resin obtained in the above (1), added was 2.7 % by mass, based on the total of the polybutadiene rubber and styrene, of a plasticizer, liquid paraffin [Idemitsu Kosan's CP50S]. These were kneaded and pelletized into pellets of the resin.

Next, the rubber-modified styrenic resin pellets were extrusion-molded into a sheet. The extrusion-molding machine used was equipped with a sheeting extruder unit [Shinko Kikai Seisakusho's EX35], a take-up unit [Tanabe Plastic Kikai's S-205-1] and a roll conditioner unit [Matsui Seisakusho's MCIII]. The resin temperature in the extruder was 230°C; and the screw revolution was 80 rpm. The lip opening of the die was 0.7 mm; and the roll temperature was 80°C, controlled by the roll controller. The rubber-modified styrenic resin sheet thus obtained herein had a thickness of 0.5 mm.

(3) Evaluation of rubber-modified styrenic resin sheet:

The rubber-modified styrenic resin sheet obtained in the above (2) was fitted in a square frame having a size of 235 mm x 235 mm, and its both surfaces were heated by the use of a thermoforming machine [Asano Laboratory's FK-0431-10]. The heater temperature was 360°C; the uppermost limit of the temperature of the sheet heated was 200°C; and the heating rate was 180°C/min. Based on the point at which the sheet shrank back, the time (sec) taken by the sheet before its center drew down by 1 cm was measured. The measurement was repeated 5 times in all, and the five data thus obtained were averaged. The thus-averaged 1 cm drawdown time (sec) of the sheet was 20.5 seconds.

Accordingly, it is understood that the 1 cm drawdown time (sec) of the sheet is larger than the defined parameter $[(MwL/10^4) - 4.0]$ of being 20 seconds.

The rubber-modified styrenic resin sheet obtained in the above (2) was thermoformed into tray containers in a mode of vacuum-pressure thermoforming. Since the sheet ensured a satisfactorily long time for its thermoforming, stable production of tray containers from it was possible. The tray containers obtained herein all had a uniform thickness, and presented a good appearance with neither surface roughness nor wrinkles that might be caused by drawdown of the sheet. The design of the mold used was well transferred onto the tray containers.

The results are given in Table 1.

[Comparative Example 1]

(1) Production of rubber-modified styrenic resin:

To a styrene solution containing 7.0 % by mass of a rubbery polymer, polybutadiene rubber [Ube Kosan's BR15HB], added were 350 ppm, in terms of its pure product and based on styrene, of a polyfunctional initiator, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane [Nippon Yushi's Perhexa 3M], 120 ppm, based on styrene, of a chain transfer agent, n-dodecylmercaptan (from Nippon Yushi), and 500 ppm, based on the total of the starting materials, of an antioxidant [Ciba-Geigy's Irganox 245).

The starting solution thus prepared was continuously fed into a first polymerization reactor of a type for complete admixture having a capacity of 20 liters (its inside was kept at 100°C) at a feed rate of 16 liters/hr. Next, the polymer formed in the first polymerization reactor was led into a second polymerization reactor of a type for complete admixture having a capacity of 20 liter, then into a third, plug-assisted flow polymerization reactor having a capacity of 30 liters, and finally into a fourth, plug-assisted flow polymerization reactor having a capacity of 30 liters in that order. In these, the polymerization temperature was kept falling between 105°C and 150°C, and the starting solution was polymerized to attain a final conversion of at least 70 %.

the total of the polybutadiene rubber and styrene.

(3) Evaluation of rubber-modified styrenic resin sheet:

The 1 cm drawdown time (sec) of the rubber-modified styrenic resin sheet obtained in the above (2) was measured in the same manner as in (3) in Example 1, and it was 19.0 seconds.

Accordingly, it is understood that the 1 cm drawdown time (sec) of the sheet is smaller than the defined parameter $[(MwL/10^4) - 4.0]$ of being 20 seconds.

The rubber-modified styrenic resin sheet obtained in the above (2) was thermoformed into tray containers in a mode of vacuum-pressure thermoforming. The fine pattern of the design of the mold used could not be well transferred onto some tray containers formed herein.

The results are given in Table 1.

[Example 2]

(1) Production of rubber-modified styrenic resin:

A rubber-modified styrenic resin was produced in the same manner as in (1) in Example 1. In this, however, the amount of the polyfunctional initiator, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane added was 500 ppm in terms of its pure product and based on styrene; and the amount of the chain transfer agent, n-dodecylmercaptan added was 150 ppm based on styrene.

(2) Production and evaluation of rubber-modified styrenic

(The following musical notation is transcribed from the image, showing various notes, rests, and bar lines across multiple staves.)

In the same manner as in (2) and (3) in Example 1, the rubber-modified styrenic resin obtained in the above (1) was pelletized and molded into a sheet, and the sheet was evaluated. In this, however, the amount of the plasticizer, liquid paraffin added to the resin was 3.2 % by mass based on the total of the polybutadiene rubber and styrene.

The results are given in Table 1.

[Example 3]

(1) Production of rubber-modified styrenic resin:

A rubber-modified styrenic resin was produced in the same manner as in (1) in Example 1. In this, however, used was a styrene solution containing 6.0 % by mass of a rubbery polymer, polybutadiene rubber [Asahi Chemical's NF55AE].

(2) Production and evaluation of rubber-modified styrenic resin sheet:

In the same manner as in (2) and (3) in Example 1, the rubber-modified styrenic resin obtained in the above (1) was pelletized and molded into a sheet, and the sheet was evaluated. In this, however, the amount of the plasticizer, liquid paraffin added to the resin was 2.1 % by mass based on the total of the polybutadiene rubber and styrene.

The results are given in Table 1.

[Example 4]

(1) Production of rubber-modified styrenic resin:

A rubber-modified styrenic resin was produced in the same manner as in (1) in Example 1. In this, however, the amount of the polyfunctional initiator, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane added was 300 ppm in terms of its pure product and based on styrene; and the amount of the chain transfer agent, n-dodecylmercaptan added was 200 ppm based on styrene.

(2) Production and evaluation of rubber-modified styrenic resin sheet:

In the same manner as in (2) and (3) in Example 1, the rubber-modified styrenic resin obtained in the above (1) was pelletized and molded into a sheet, and the sheet was evaluated. In this, however, the amount of the plasticizer, liquid paraffin added to the resin was 1.0 % by mass based on the total of the polybutadiene rubber and styrene.

The results are given in Table 1.

[Comparative Example 2]

(1) Production of rubber-modified styrenic resin:

To a styrene solution containing 7.0 % by mass of a rubbery polymer, polybutadiene rubber [Ube Kosan's BR15HB], added was 500 ppm, based on the total of the starting materials, of an antioxidant [Ciba-Geigy's Irganox 245]. To this, however, a polymerization initiator and a chain transfer agent were not added. The starting solution thus prepared was polymerized in the same manner as in Comparative Example 1 to

obtain a rubber-modified styrenic resin. In this, however, the feed rate of the solution to the first polymerization reactor of a type for complete admixture was 16 liters/hr, and the temperature inside the first polymerization reactor was kept at 120°C.

The continuous phase of the rubber-modified styrenic resin obtained herein had a linear weight-average molecular weight (MwL) of 207,000. It had a degree of branching of 0.0 for its absolute molecular weight (M_B) of 1,000,000 measured in GPC/LALLS.

(2) Production of rubber-modified styrenic resin sheet:

The rubber-modified styrenic resin obtained in the above (1) was molded into a sheet in the same manner as in (2) in Example 1. In this, however, the amount of the plasticizer, liquid paraffin added to the resin was 1.0 % by mass based on the total of the polybutadiene rubber and styrene.

(3) Evaluation of rubber-modified styrenic resin sheet:

The 1 cm drawdown time (sec) of the rubber-modified styrenic resin sheet obtained in the above (2) was measured in the same manner as in (3) in Example 1, and it was 15.0 seconds.

Accordingly, it is understood that the 1 cm drawdown time (sec) of the sheet is smaller than the defined parameter $[(MwL/10^4) - 4.0]$ of being 16.7 seconds.

The rubber-modified styrenic resin sheet obtained in

the above (2) was thermoformed into tray containers in a mode of vacuum-pressure thermoforming. Some tray containers formed herein were defective in that their thickness was partly thinned. Their appearance was not good, and their mechanical strength was low.

The results are given in Table 1.

[Example 5]

(1) Production of rubber-modified styrenic resin:

A rubber-modified styrenic resin was produced in the same manner as in (1) in Example 1. In this, however, 60 ppm, in terms of its pure product and based on styrene, of an unsaturated compound having a plurality of double bonds, divinylbenzene (from Wako Pure Chemical) of 55 % purity was added to the styrene solution in place of the polyfunctional initiator; and the chain transfer agent was not added thereto. The temperature inside the first polymerization reactor of a type for complete admixture was kept at 120°C.

(2) Production and evaluation of rubber-modified styrenic resin sheet:

In the same manner as in (2) and (3) in Example 1, the rubber-modified styrenic resin obtained in the above (1) was pelletized and molded into a sheet, and the sheet was evaluated. In this, however, the amount of the plasticizer, liquid paraffin added to the resin was 1.0 % by mass based on the total of the polybutadiene rubber and styrene.

[illegible]

(1) Production of rubber-modified styrenic resin:

The amount of the polyfunctional initiator, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane to be added to the styrene solution was converted to 1000 ppm based on styrene, and the process (1) of Example 1 was tried to produce a rubber-modified styrenic resin. However, the viscosity of the reaction mixture increased too much, and removing the heat from the reactor was difficult. As a result, the temperature of the reaction system could not be controlled, and feeding the reaction liquid to the next stage was impossible.

Table 1

Example (Comparative Example)	Weight-average Molecular Weight $\times 10^4$	Degree of Branching	1 cm Drawdown Time (sec)
1	24.0	0.5	20.5
(1)	24.0	0.0	19.0
2	25.5	0.8	23.0
3	23.0	0.5	21.2
4	21.0	0.4	19.5
(2)	20.7	0.0	15.0
5	24.0	0.9	24.5

INDUSTRIAL APPLICABILITY

The present invention provides a rubber-modified styrenic resin having the advantage of good thermoforming stability. When the resin sheet is thermoformed in vacuum or under pressure into secondary products, it ensures a sufficiently long time for its thermoforming, as its drawdown time is long. The invention also provides an effective method

for producing the resin, and also a sheet of the resin.

CLAIMS

1. A rubber-modified styrenic resin with particles of a rubbery polymer dispersed therein, which is characterized in that its continuous phase has a weight-average molecular weight (MwL) falling between 180,000 and 280,000, and that the weight-average molecular weight (MwL) and the 1 cm drawdown time (sec) of the resin sheet satisfy the following formula:

$$1 \text{ cm drawdown time (sec)} > (MwL/10^4) - 4.0.$$

2. The rubber-modified styrenic resin as claimed in claim 1, of which the continuous phase has a degree of branching of from 0.2 to 1.0 for its absolute molecular weight of 1,000,000 measured in GPC/LALLS.

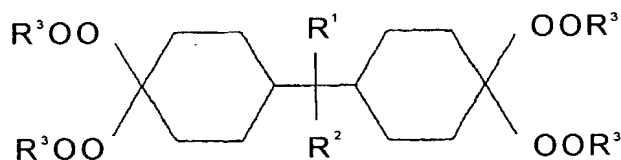
3. The rubber-modified styrenic resin as claimed in claim 1 or 2, of which the rubbery polymer content falls between 3 and 12 % by mass.

4. A method for producing a rubber-modified styrenic resin of any of claims 1 to 3 by polymerizing a rubbery polymer and a monomer component consisting essentially of a styrenic monomer in the presence of a polyfunctional initiator, wherein the amount of the polyfunctional initiator falls between 50 and 500 ppm relative to the monomer component consisting essentially of a styrenic monomer.

5. The method for producing a rubber-modified styrenic resin as claimed in claim 4, wherein the amount of the polyfunctional initiator falls between 100 and 500 ppm relative

to the monomer component consisting essentially of a styrenic monomer.

6. The method for producing a rubber-modified styrenic resin as claimed in claim 4 or 5, wherein the polyfunctional initiator is a tetrafunctional organic compound of the following general formula:



wherein R^1 and R^2 each represent a hydrogen atom or an alkyl group having 1 or 2 carbon atoms; and R^3 represents an alkyl group having from 1 to 8 carbon atoms.

7. The method for producing a rubber-modified styrenic resin as claimed in any of claims 4 to 6, wherein the polyfunctional initiator is 2,2-bis(4,4-di-*t*-butylperoxycyclohexyl)propane.

8. A method for producing a rubber-modified styrenic resin of any of claims 1 to 3 by polymerizing a rubbery polymer and a monomer component consisting essentially of a styrenic monomer in the presence of an unsaturated compound having a plurality of copolymerizing double bonds, wherein the amount of the unsaturated compound falls between 50 and 250 ppm relative to the monomer component consisting essentially of

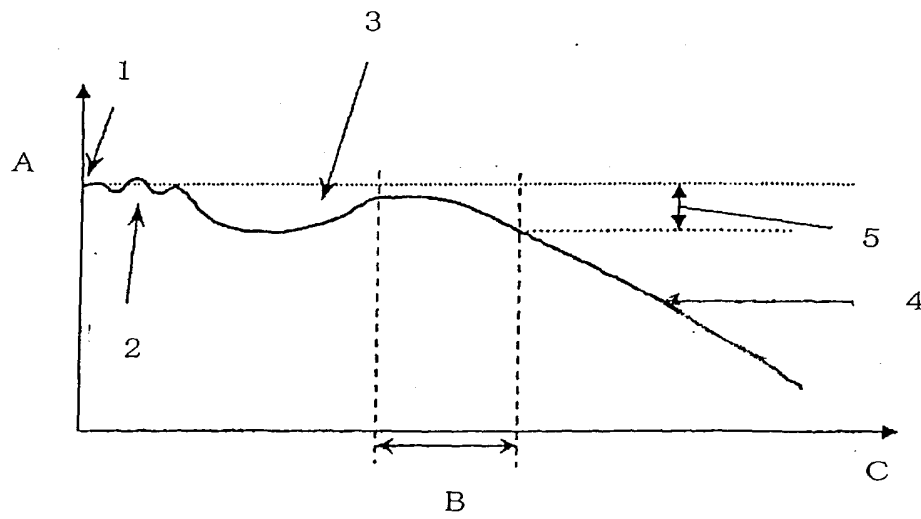
a styrenic monomer.

9. A rubber-modified styrenic resin sheet prepared by molding the rubber-modified styrenic resin of any of claims 1 to 3.

ABSTRACT

Provided is a rubber-modified styrenic resin with particles of a rubbery polymer dispersed therein. The continuous phase of the resin has a weight-average molecular weight (MwL) falling between 180,000 and 280,000, and its weight-average molecular weight and the 1 cm drawdown time (sec) of the resin sheet satisfy a formula, $1 \text{ cm drawdown time (sec)} > (\text{MwL}/10^4) - 4.0$. Also provided are an effective method for producing the resin, and a rubber-modified styrenic resin sheet produced by molding the resin. The resin is suitable for molding it into sheets. The resin sheet ensures a satisfactorily long time for its thermoforming, and therefore has good thermoforming stability.

Fig. 1



Declaration, Power Of Attorney and Petition

Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

RUBBER-MODIFIED STYRENIC RESIN, METHOD FOR PRODUCING IT AND SHEET OF
THE RESIN

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____

☒ was filed as PCT international application

Number PCT/JP00/07277

on October 19, 2000

and was amended under PCT Article 19

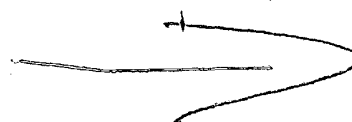
on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
<u>11-296489</u>	<u>Japan</u>	<u>19/10/1999</u>	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No



We (I) hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365 (c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Status (pending, patented,

Application Serial No.

Filing Date

abandoned)

And we (I) hereby appoint: Norman F. Oblon, Reg.No.24,618; Marvin J. Spivak, Reg.No.24,913; C. Irvin McClelland, Reg.No.21,124; Gregory J. Maier, Reg.No.25,599; Arthur I. Neustadt, Reg.No.24,854; Richiard D. Kelly, Reg.No.27,757; James D. Hamilton, Reg.No.28,421; Eckhard H. Kuesters, Reg.No.28,870; Robert T. Pous, Reg.No.29,099; Chiarles L. Gholz, Reg.No.26,395; Vincent J. Sunderdick, Reg.No.29,004; William E. Beaumont, Reg.No.30,996; Robert F. Gnuse, Reg.No.27,295; Jean-Paul Lavalleye, Reg.No.31,451; Stephen G. Baxter, Reg.No.32,884; Robert W. Hahl, Reg.No.33,893; Richiard L. Chinn, Reg.No.36,379; Steven P. Weihrouch, Reg.No.32,829; John T. Goolkasian, Reg.No.26,142; Richiard L. Chinn, Reg.No.34,305; Steven E. Lipman, Reg.No.30,001; Carl E. Schlier, Reg.No.34,426; James J. Kulbaski, Reg.No.34,648; Richiard A. Neifeld, Reg.No.35,299; J.Derek Mason, Reg. No.35,270; Surinder Sachar, Reg. No.34,423; Christina M. Gadiano, Reg. No.37,628; Jeffrey B. McIntyre, Reg.No.36,867; Paul E. Rauch, Reg.No.38,591; William T Enos, Reg.No.33,128; and Micheal E. McCabe, Jr., Reg.No.37,182; our(my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we(I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C., whose Post Office Address is Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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